

# Heat Content of Molybdenum Disilicide From 0° to 900° C<sup>1</sup>

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The heat content relative to 0° C of a sample of molybdenum disilicide (MoSi<sub>2</sub>) was measured at 100-degree intervals up to 900° C, using a nichrome-V container for the sample, a silver-core furnace, and a precision ice calorimeter. Corrections were applied for the impurities (approximately 2 percent) reported to be in the sample. The equation

$$H_t - H_0 = 0.48560t + 3.586(10^{-5})t^2 - 41.78 \log_{10}[(t + 273.16)/273.16],$$

giving between 0° and 900° C the heat content in absolute joules per gram at  $t^\circ$  less than that at 0° C, represents the unsmoothed corrected mean values, with an average deviation of 0.24 absolute joule gram<sup>-1</sup>. This equation is believed to have an absolute accuracy within 2 percent between 100° and 800°. Values of the relative heat content, heat capacity, and relative entropy derived from this equation are formulated and tabulated at even temperatures.

## 1. Introduction

There are several compounds of molybdenum and silicon, of which the best known is the disilicide. This substance has considerable resistance to oxidation, and because of this and other properties, shows promise as a high-temperature structural material. No measurements of its heat capacity were found in the literature.

## 2. Experimental Procedure

The sample of molybdenum disilicide, broken into pieces of about 2- or 3-mm diameter, was furnished by the Lewis Flight Propulsion Laboratory, National Advisory Committee for Aeronautics, Cleveland, Ohio. This laboratory stated that the impurities were approximately as follows: Iron, 0.8 percent; oxygen, 0.50 percent; nitrogen, 0.34 percent; and carbon, 0.17 percent.

A preliminary test of a separate portion of the sample was conducted to determine its apparent behavior at high temperatures toward oxygen and toward nichrome V, in anticipation of using the latter as a container material. Simple heating at about 1,000° C for a few minutes on a nichrome plate in air gave no obvious evidence of oxidation of the MoSi<sub>2</sub> nor of its attack of the nichrome.

The method and apparatus employed for the heat-content measurements were described in detail in an earlier paper.<sup>2</sup> Briefly, the procedure involved heating the sample, in its helium-filled container of nichrome V, to a known temperature in the furnace. The sample and container were then dropped into the ice calorimeter, which measured the heat delivered in cooling to 0° C. Repetition of the same procedure on the empty container measured the part of the heat that had not been delivered by the sample itself. From such measurements of relative heat

content at a sufficient number of furnace temperatures, the heat capacity over the temperature range covered can be derived by one of the usual methods.

The furnace temperature was measured up to 600° C by a platinum resistance thermometer, and above 600° by a platinum-platinum-10-percent-rhodium thermocouple. The calibration factor of the ice calorimeter, as determined earlier by numerous electrical calibrations, and with the same apparatus, is 270.48 abs j/g Hg.<sup>3</sup>

## 3. Heat-Content Data and Corrections Applied

Several very small corrections to the measured heats were made whenever significant, especially for the small heat leak of the calorimeter (usually about 2 j/hr) and for slightly varying masses of container materials entering the calorimeter. Two major corrections, however, had to be applied. These were (a) for increases in weight of the container itself, totaling several milligrams throughout the series of measurements, due to oxidation at the higher temperatures by traces of oxygen in the furnace atmosphere, and (b) for the impurities in the sample of molybdenum disilicide listed in section 2.

The corrections for oxidation of the container were computed from the differences in heat content of Fe<sub>3</sub>O<sub>4</sub> and metallic iron.<sup>4</sup> The corrections themselves were relatively small (in no instance exceeding 0.7 percent of the total heat measured), and should be sufficiently accurate for this purpose, as the increase in heat content during oxidation of iron or one of the metals composing nichrome V depends largely on the amount of oxygen acquired, regardless of which metal is involved or which of its oxides is formed.

<sup>3</sup> The factor, differing slightly from the previously published value of 270.46 (footnote 2), was arrived at by a correction of the circuit constants applicable in all the calibration experiments.

<sup>4</sup> K. K. Kelley, Contributions to the data on theoretical metallurgy, X. Entropy data for inorganic compounds, U. S. Bureau of Mines Bulletin 476, U. S. Government Printing Office, Washington 25, D. C., 1949.

<sup>1</sup> This work was supported by the United States Air Force, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

<sup>2</sup> D. C. Ginnings, T. B. Douglas, and Anne F. Ball, J. Research NBS **45**, 23 (1950) RP2110.

The heats found were corrected for the approximately 2 percent of reported impurities by calculating in a similar way the approximate differences in heat content that would occur were the impurities replaced by the same mass of pure molybdenum disilicide. Taking advantage of the roughly approximate equality of the gram-atomic heat capacities of many elements at temperatures not too low, the effects of the impurities oxygen, nitrogen, and carbon were corrected for as though these elements were present in the form of the same total number of gram atoms of oxygen only, and in the manner described above. The effect of the impurity iron was corrected for, using the heat-content values of this element given by Kelley (see footnote 4). Making the total correction for the impurities at each furnace temperature was equivalent to decreasing the net measured heat content of the molybdenum disilicide sample by approximately 3 percent. The greatest part of this correction can be attributed to the fact that the average atomic weight of the impurity content is much smaller than that of MoSi<sub>2</sub>.

The corrected measured heats from individual runs are given in table 1 in absolute joules, and at each temperature in the chronological order in which they were obtained. The mass of molybdenum disilicide was 16.560 g in each case. For each temperature the last three columns afford a comparison between the observed mean net heat content per gram and the corresponding smoothed value calculated as described in section 4.

TABLE 1. Individual heat content measurements

Furnace temperature <i>t</i>	Measured heat		Mean net heat content of MoSi <sub>2</sub> , $H_t - H_0$		
	Sample and container	Empty container	Observed	Calculated	Difference
$^{\circ}\text{C}$	<i>abs j</i>	<i>abs j</i>	<i>abs j g<sup>-1</sup></i>	<i>abs j g<sup>-1</sup></i>	<i>abs j g<sup>-1</sup></i>
100.0	{ 1245.7 1243.2 }	<sup>a</sup> 535.6	42.81	43.26	-0.45
150.0	{ 816.4 815.4 }				
200.0	{ 2573.7 2572.7 }	<sup>a</sup> 1101.9	88.85	88.59	+0.26
300.0	{ <sup>b</sup> (3950.7) 3939.5 3939.7 3939.3 }	{ 1689.0 1696.1 1702.3 1684.6 1693.6 1696.1 2316.8 2306.2 2316.1 2306.7 }	135.62	135.46	+ .16
400.0	{ 5351.2 5351.6 }	{ 2316.8 2306.2 2316.1 2306.7 }	183.57	183.61	- .04
500.0	{ 6791.0 6794.1 6787.8 8262.8 8266.9 8281.7 8286.8 8278.1 9847.5 9853.4 9842.9 }	{ 2933.4 2931.4 3590.8 3590.0 3593.3 3590.1 }	233.01	232.89	+ .12
600.0	{ 8262.8 8266.9 8281.7 8286.8 8278.1 9847.5 9853.4 9842.9 }	{ 3590.8 3590.0 3593.3 3590.1 }	282.87	283.18	- .31
701.7	{ 11349.8 11343.7 }	{ 4298.6 4298.7 }	335.11	335.32	- .21
796.2	{ 12934.3 12936.5 }	{ 4975.1 4967.5 4969.7 5694.7 5700.7 5696.6 }	385.03	384.60	+ .43
895.5			437.09	437.24	- .15

<sup>a</sup> Not measured directly, but found by interpolation.

<sup>b</sup> Excluded from the mean because of inferior precision.

## Heat Content, Heat Capacity, and Entropy

The corrected smooth values of the heat content of molybdenum disilicide, in excess of that at 0°C, are represented from  $t=0^{\circ}$  to  $t=900^{\circ}\text{C}$  by the equation (in absolute joules per gram)

$$H_t - H_0 = 0.48560t + 3.586(10^{-5})t^2 - 41.78 \log_{10}[(t+273.16)/273.16], \quad (1)$$

whose coefficients were found by least squares from the observed values of the fourth column of table 1. Differentiation of eq (1) gives the heat capacity (in absolute joules per gram deg C)

$$C_p = 0.4856 + 7.17(10^{-5})t - 18.14/(t+273.16). \quad (2)$$

Values of heat content calculated from eq (1) are listed in the fifth column of table 1, and smoothed values of heat capacity calculated from eq (2) are listed in table 2.

Figure 1 affords a graphical comparison between the heat capacity in calories per gram-atom degree C,<sup>5</sup> as calculated from eq (2), and the "observed" values calculated from successive differences of mean

<sup>5</sup> One gram-atom of MoSi<sub>2</sub> (50.71 g)=one-third the gram-molecular-weight. One calorie=4.1840 abs j.

TABLE 2. Heat capacity of molybdenum disilicide

Temperature	Heat capacity	Temperature	Heat capacity
$^{\circ}\text{C}$	<i>abs j g<sup>-1</sup> deg C<sup>-1</sup></i>	$^{\circ}\text{C}$	<i>abs j g<sup>-1</sup> deg C<sup>-1</sup></i>
0	0.419	500	0.498
50	.433	550	.503
100	.444	600	.508
150	.453	650	.513
200	.462	700	.517
250	.469	750	.522
300	.476	800	.526
350	.482	850	.531
400	.487	900	.535
450	.493		

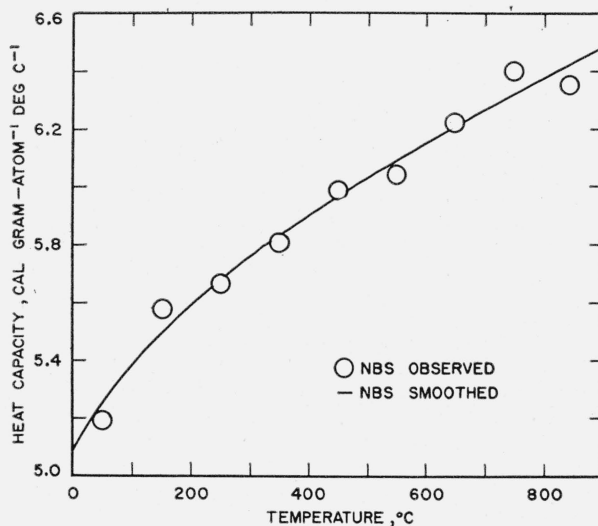


FIGURE 1. Heat capacity of molybdenum disilicide.

heat content given in the fourth column of table 1. Very small corrections for curvature<sup>6</sup> have been applied to the latter values. The heat-capacity values of figure 1 may be compared with 6.3 cal/g-atom deg C, a value that holds approximately for a large number of chemical elements and compounds at these temperatures. This simple generalization, which is very useful for rough estimates, predicts too high a heat capacity at room temperature for substances containing elements of low atomic weight (even silicon), as the tendency for the Debye temperatures to be unusually high in these cases causes the heat capacities to approximate this predicted value only at higher temperatures.

The precision of measuring the net heat content of molybdenum disilicide at any given temperature, as determined by the variation of individual measurements recorded in table 1, corresponded to a probable error of the mean averaging  $\pm 0.05$  percent. The corresponding probable error of the mean "observed" heat-capacity values calculated from the enthalpy values at two successive furnace temperatures was found to average  $\pm 0.35$  percent. The difference between these "observed" heat capacities and those given by eq (2) average 0.8 percent. Considering also the possible systematic errors, it is believed that the absolute error of eq (1) does not exceed 2 percent between 100° and 800° C.

The increased uncertainty in evaluating a derivative (here the heat capacity) near the ends of the range of measurement is exemplified by comparison of eq (2) with the best corresponding quadratic equation, the disagreement between the two equations being less than 0.5 percent between 100° and 800° but amounting to 1.7 percent at 0°. The best quadratic equation fits the "observed" values with the same average deviation as eq (2), but has a less

plausible form, as it would lead to a maximum in the heat capacity at some temperature above 900°.

Taking the "molecular weight" of MoSi<sub>2</sub> as 152.13, equations for the relative heat content, relative entropy, and heat capacity may be readily derived from eq (1). In terms of calories mole<sup>-1</sup> and at T° K, these equations are as follows:

$$H_T^\circ - H_{298.16}^\circ = 16.944T + 0.001304T^2 - 1519.2 \log_{10} T - 1409; \quad (3)$$

$$S_T^\circ - S_{298.16}^\circ = 39.016 \log_{10} T + 0.00261T + 660/T - 99.53; \quad (4)$$

$$C_p^\circ = 16.94 + 0.00261T - 660/T. \quad (5)$$

Values up to 1,200° K, calculated from eq (3), (4), and (5), are given in table 3.

TABLE 3. Heat content, heat capacity, and relative entropy of MoSi<sub>2</sub>

T	$H_T^\circ - H_{298.16}^\circ$	$C_p^\circ$	$S_T^\circ - S_{298.16}^\circ$
° K	cal mole <sup>-1</sup>	cal mole <sup>-1</sup> deg K <sup>-1</sup>	cal mole <sup>-1</sup> deg K <sup>-1</sup>
298.16	0	15.50	0.00
300	28	15.52	.10
350	816	15.97	2.53
400	1,624	16.33	4.69
450	2,449	16.65	6.63
500	3,289	16.92	8.40
550	4,142	17.18	10.02
600	5,006	17.41	11.53
650	5,882	17.62	12.93
700	6,768	17.82	14.24
750	7,665	18.02	15.48
800	8,570	18.20	16.65
850	9,485	18.38	17.76
900	10,409	18.56	18.82
950	11,341	18.72	19.82
1,000	12,281	18.89	20.79
1,050	13,230	19.05	21.71
1,100	14,187	19.21	22.60
1,150	15,151	19.37	23.46
1,200	16,124	19.52	24.29

<sup>6</sup> N. S. Osborne, H. F. Stimson, T. S. Sligh, and C. S. Cragoe, BS Sci. Pap. 20, 65 (1925) S501.

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